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STUDIES ON THE REMOVAL OF CARBON MONOXIDE FROM THE ATMOSPHERE A--ETC(11)

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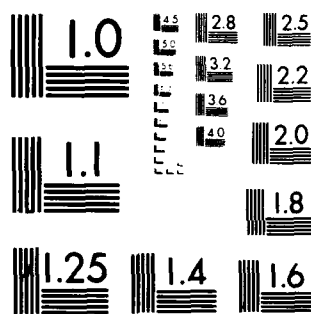
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**Studies on the Removal of Carbon Monoxide From the Atmosphere at Ambient Temperature.**

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by  
Dwight A. Fine  
Carl A. Moller  
Research Department

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**NAVAL WEAPONS CENTER  
CHINA LAKE, CALIFORNIA 93555**

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### FOREWORD

This is a final report on two projects funded by the Naval Sea Systems Command in 1979. The two tasks were N00024-79-WR-9G15 and 50205-SL, both under program element 63561N. The program is part of an effort to develop effective methods for removal of contaminants from submarine atmospheres during emergency situations when the purification methods normally employed may be inoperative.

This report was reviewed for technical accuracy by William R. McBride.

Approved by  
E. B. ROYCE, *Head*  
*Research Department*

Under authority of  
W. B. HAFF  
CAPT., U. S. Navy  
*Commander*

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Subj: NWC TP 6179, *Studies on the Removal of Carbon Monoxide from the Atmosphere at Ambient Temperature*, dated May 1980; errata for

1. Please substitute the following legend for Figure 4 on page 12 of subject report:

FIGURE 4. Removal of CO from CO/N<sub>2</sub> and CO/Air by 1.0 gm 5% palladium on alumina powder.

*J. M. Buege for*  
ALBERTA L. COX

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(U) *Studies on the Removal of Carbon Monoxide From the Atmosphere at Ambient Temperature*, by Dwight A. Fine and Carl A. Heller. China Lake, Calif., Naval Weapons Center, May 1980. 22 pp. (NWC TP 6179, publication UNCLASSIFIED.)

(U) Catalysts of platinum or palladium on carbon or alumina show much promise in removing carbon monoxide (CO) from air at room temperature. As much as 80% of the CO in a 230 ppm CO/air mixture was removed by 1 g of 5% palladium on carbon powder in one pass. Catalysts of 0.5% metal on alumina pellets showed comparable efficiency, and proved much more convenient to handle. Calculations indicate that the CO concentration in 1000 ft<sup>3</sup> of air containing 500 ppm CO could be reduced to 200 ppm in 100 minutes using only 180 g (0.4 pound) of 0.5% palladium catalyst and a pump moving 10 ft<sup>3</sup> per minute of air (one pass of air through catalyst). Solutions of copper(I) in monoethanolamine proved much less efficient due to oxidation problems.

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Dr. Frank Ventriglio of the Naval Sea Systems Command and Drs. Fred Saalfeld and James DeCorpo of the Naval Research Laboratory gave us much useful information. Mr. William Dell of Beckman Instruments suggested the platinum metal catalysts and Mr. Paul Nayurnik of Engelhard Industries supplied us with free samples of several catalysts.



## INTRODUCTION

This report summarizes the work performed in FY 1979 and 1980 on an investigation of removal of carbon monoxide (CO) from submarine atmospheres at ambient temperatures, sponsored by the Naval Sea Systems Command (NAVSEA).

Normally, CO is removed from submarine atmospheres by high temperature combustion to the dioxide. A drastic increase in CO concentration from an emergency such as fire, combined with a loss of power such as to render the CO burners inoperable, could produce dangerously high, perhaps lethal concentrations of CO. There is need for a process that could operate at room temperature to reduce the concentration to a tolerable level.

Information regarding safe concentrations of CO, and concentrations that might be expected in case of various emergencies, was obtained from Dr. Frank Ventriglio of NAVSEA and from Drs. Fred Saalfeld and James DeCorpo of the Naval Research Laboratory (NRL). A limit of 15 ppm has been set by the Bureau of Medicine (BUMED) for the concentration tolerable in a submarine under normal conditions for periods up to 90 days. In the event of an emergency which raises the concentration, 200 ppm could be tolerated for 24 hours assuming no exertion, 500 ppm could be tolerated for 100 minutes, 1000 ppm for 60 minutes. Submarines make use of a carbon bed for removal of organic contaminants; a fire in this carbon bed could produce CO at the rate of 1000 ppm per minute, and 500 ppm could still be produced after the fire was put out. The scenario calls for reducing the CO level from 5000 ppm to 50 ppm, and maintaining the level at no more than 50 ppm for 72 hours with the burner inoperative.

Submarines now have emergency circulators throughout their compartments for the removal of carbon dioxide. We do not have quantitative information about these emergency items, but have spoken with submariners who described their use and size. The ideal use of CO-removing materials would be in these emergency circulators, and preferably in volumes small enough so that design changes would not be required.

A survey of the literature indicated two general types of possibilities for removal of CO at room temperature: (1) chemical absorption by

solutions or solids, where the absorbing materials could later be regenerated, (2) catalytic oxidation to CO<sub>2</sub>.

Carbon monoxide has long been known to be absorbed quantitatively by certain solutions containing copper(I).<sup>1</sup> These solutions include aqueous solutions of chlorocuprates(I), aqueous ammonia solutions of cuprous chloride, and solutions of cuprous chloride in water/ethanol-amine mixtures. The gas is absorbed to the extent of one molecule of CO per atom of Cu. Recent work has demonstrated that the principal species formed in aqueous HCl solution is Cu(CO)Cl<sub>2</sub><sup>-</sup>.<sup>2</sup>

Aqueous solutions possess disadvantages for the present purpose, because of the need to employ hydrochloric acid or ammonia and the susceptibility of copper(I) to air oxidation. Ethanolamine solutions of cuprous chloride are known to absorb CO, but have not been employed or investigated extensively due to lack of economic advantage over acid or ammoniacal solutions. Ethanolamine is presently employed in scrubbers on submarines for removal of carbon dioxide, by formation of a 2:1 amine:CO<sub>2</sub> adduct. Addition of cuprous chloride to the scrubber solution might provide a means for temporary removal of CO as well as CO<sub>2</sub>.

Oxidation catalysts are well known; in fact, the present oxidation chambers in submarines use a catalyst to oxidize CO and hydrocarbons. An elevated temperature is employed, possibly because of the hydrocarbons and the presence of various catalyst poisons. For a short emergency period, catalysts operating at ambient temperature might serve the purpose. The reaction of interest is:



One candidate for such a catalyst is thorium oxide (ThO<sub>2</sub>), which is mentioned in a brief article on cataluminescence.<sup>3</sup> Reaction (1) was said to proceed at "low" temperatures and the ThO<sub>2</sub> was reported to glow. This was intriguing, since the ThO<sub>2</sub> might serve both to remove CO and to monitor the presence of CO, if a phototube was used to view the ThO<sub>2</sub> surface.

<sup>1</sup> For a review article, see M. J. Bruce, *J. Organometallic Chem.*, Vol. 44 (1972), p. 209.

<sup>2</sup> M. A. Busch and T. C. Franklin, *Inorg. Chem.*, Vol. 18 (1979), p. 521.

<sup>3</sup> F. F. Vol'kenshtein, *Kinetika i Kataliz.*, Vol. 19 (1977), p. 90. Translation by Plenum (1978).

In conversation with technical representatives from Beckman Instruments (William Dell and William Clarke), mention was made of catalysts produced by Engelhard Industries which remove CO efficiently at room temperature. These catalysts, consisting of platinum metals supported on carbon or alumina, have found a wide variety of applications, and have been employed recently by the automobile industry for purification of exhaust gases. Eleven samples of these catalysts were obtained from Engelhard.

#### EQUIPMENT AND TECHNIQUES

Carbon monoxide concentration was monitored by a Beckman Model 865 CO analyzer. Air/CO and nitrogen/CO mixtures were purchased from Scientific Gas Products. The value of the CO concentration given by the company was used to calibrate the analyzer.

Reagents employed in the tests of copper(I) solutions were obtained from commercial sources and used without further purification.

The apparatus used in the tests is shown schematically in Figure 1. The system was a circulating system which could be filled with a mixture of air/CO or nitrogen/CO. After the system was stable, the absorbing material being tested was placed in the circuit and the CO concentration was monitored. The apparatus was made of rubber tubing and glass vessels. The pump was a single-speed pump and the flow rate was governed by that speed and the back pressure.

#### PRELIMINARY TESTS, WITHOUT CO ANALYZER

Delays in filling the order for a Beckman CO analyzer led us to run some preliminary tests with a very simple apparatus. Thorium oxide was placed in a ceramic boat inside a quartz tube. A mixture of air and CO having a high CO concentration was passed over the ThO<sub>2</sub> powder. The tube was heated by several turns of nichrome wire and a Variac; the temperature of the catalyst was measured by a thermocouple. Runs were made in a darkened room at night, at room temperature and at 240°C and 334°C. No glow was observed visually. Later, when a reference describing the original ThO<sub>2</sub> work was found,<sup>4</sup> it was learned that the temperatures used for the catalysis were between 255 and 344°C. Thus

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<sup>4</sup> M. Breysse, B. Claudel, L. Fause, M. Guenin, R. Williams and T. Wolkenstein, *J. Catalysis*, Vol. 45 (1976), p. 137.

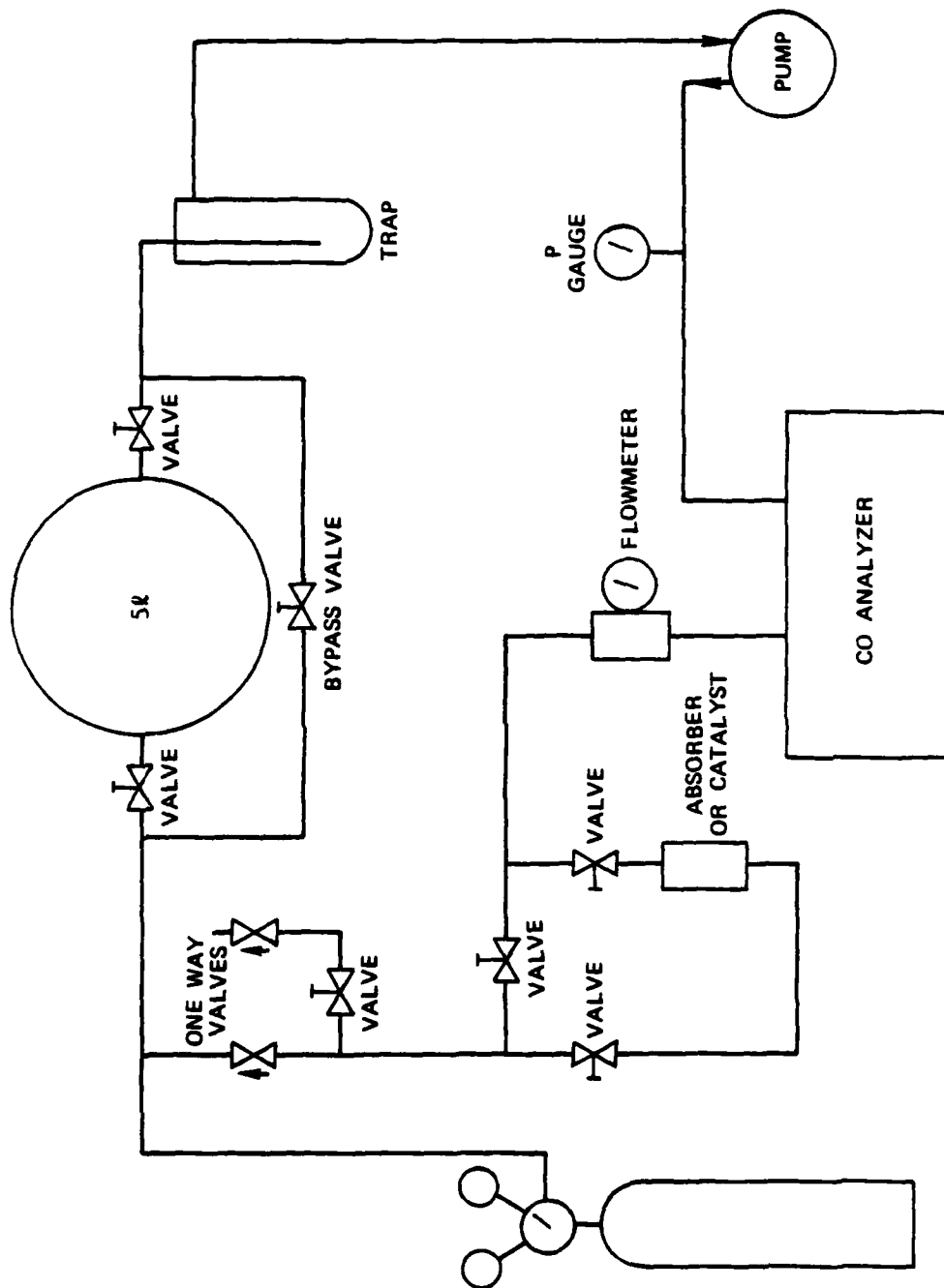


FIGURE 1. Apparatus for Testing of Absorbers and Catalysts.

the luminescence, if real, could be used as a detector, but the oxidation reaction apparently does not proceed at ambient temperature.

While still awaiting the arrival of a CO analyzer, we acquired a CO detector used by Dr. Richard Knipe of this laboratory to monitor CO for safety purposes during laser runs. This detector was incorporated into the apparatus described previously to learn if the detector could substitute temporarily for the analyzer. When a 500 ppm CO/air mixture was passed over the instrument's sensor, an off-scale reading showed on the 0-200 ppm range; when attempts were made to dilute and circulate the mixture so as to bring the reading onto scale and run a base line at about 150 ppm, the reading did not level off but fell rapidly toward zero. The company informed us that the sensor uses a "warm" oxidation catalyst and a thermocouple, and monitors CO concentration by oxidizing the CO and measuring the resultant temperature rise. A breakdown of the instrument prevented further tests.

#### TESTS OF ENGELHARD POWDERED CATALYSTS

The first materials tested after the Beckman analyzer was incorporated into the system were six catalysts obtained from Engelhard Industries. All of them contained 5% by weight of metal; they included preparations of palladium, platinum, rhodium and ruthenium on carbon powder, and of palladium on alumina powder.

For the initial tests the 5 liter flask and the trap were removed from the circuit, reducing the total volume to ca. 500 cm<sup>3</sup>. A sample of catalyst weighing 1.0 gm was placed on the frit of a sintered-glass crucible incorporated into the system. The system was filled with a CO/air mixture containing 500 ppm CO; the mixture was then pumped through the catalyst, and the CO level registered by the analyzer was noted. In all cases, the CO level was reduced to less than 5 ppm. The catalysts tested, and the time for removal of the CO are shown in the following table:

Catalyst	Approximate time for reduction of CO level to less than 5 ppm
5% Pd on carbon	30 sec
5% Pd on carbon, 50% water wet	30 sec
5% Pd on alumina	15 sec
5% Pt on carbon	15 sec
5% Rh on carbon	5 min
5% Ru on carbon	20 min

Typical curves for CO level vs. time are shown in Figure 2. It is seen from the table and figure that the order of efficiency of the different metals was  $\text{Pt} \gtrsim \text{Pd} > \text{Rh} > \text{Ru}$ .

Following these initial tests, the 5 liter flask and the trap were reincorporated into the circuit to give a total volume of approximately  $6000 \text{ cm}^3$ . The system was filled with a CO/air mixture; when the reading on the analyzer became steady, the mixture was sent through 1.0 g of catalyst. The flow rate was approximately  $4000 \text{ cm}^3$  per minute. The two catalysts tested in this manner were 5% Pd on carbon (50% water wet) and 5% Pd on alumina. Data for CO level vs. time are shown in Figure 3. It is seen that in each case, 1.5 minute was required to reduce the CO level from 240 ppm to below 50 ppm, and 2.3 minutes to reduce the level to below 5 ppm. Hence, about 83% of the total CO was removed during the time for passage of one system volume through the catalyst, and all of the detectable remainder was removed in the second pass.

While the arrival of some new CO/air mixture was being awaited, some runs were made with a CO/nitrogen mixture containing 528 ppm. Palladium catalysts, on carbon and alumina powder, were employed for the runs. It was found that CO was removed from the CO/nitrogen mixtures, but at a lower rate than from the CO/air mixtures.

This raises the question of whether the removal process is strictly catalytic oxidation, or if CO is being removed by chemisorption. Platinum metals on carbon and alumina are known to absorb CO by formation of  $\text{M}(\text{CO})$ ,  $\text{M}(\text{CO})_2$  and  $\text{M}-\text{CO}-\text{M}$  entities.<sup>5,6</sup> Such absorption would be an essential step in catalytic oxidation, but would have to be followed by reaction with oxygen. To determine whether or not the process in CO/N<sub>2</sub> was strictly absorption, calculations were made of the molar quantity of CO present in a system volume containing 528 ppm CO and of the g-atoms of metal present in 1.0 g of catalyst. Repeated runs were then made, until enough CO had been sent through the system to exhaust the capacity of the catalyst if the process were strictly absorption. No decrease in removal ability was observed. Possible sources of oxygen that would enable catalytic oxidation to take place in the CO/N<sub>2</sub> mixture are oxygen molecules adsorbed on the original catalyst, and leaks in the apparatus.

<sup>5</sup> R. P. Eischens, *Accts. Chem. Res.*, Vol. 5 (1972), p. 74.

<sup>6</sup> J. J. Yates, J. M. Duncan, D. S. Worley and R. W. Vaughan, *J. Chem. Phys.*, Vol. 70 (1979), p. 1219.

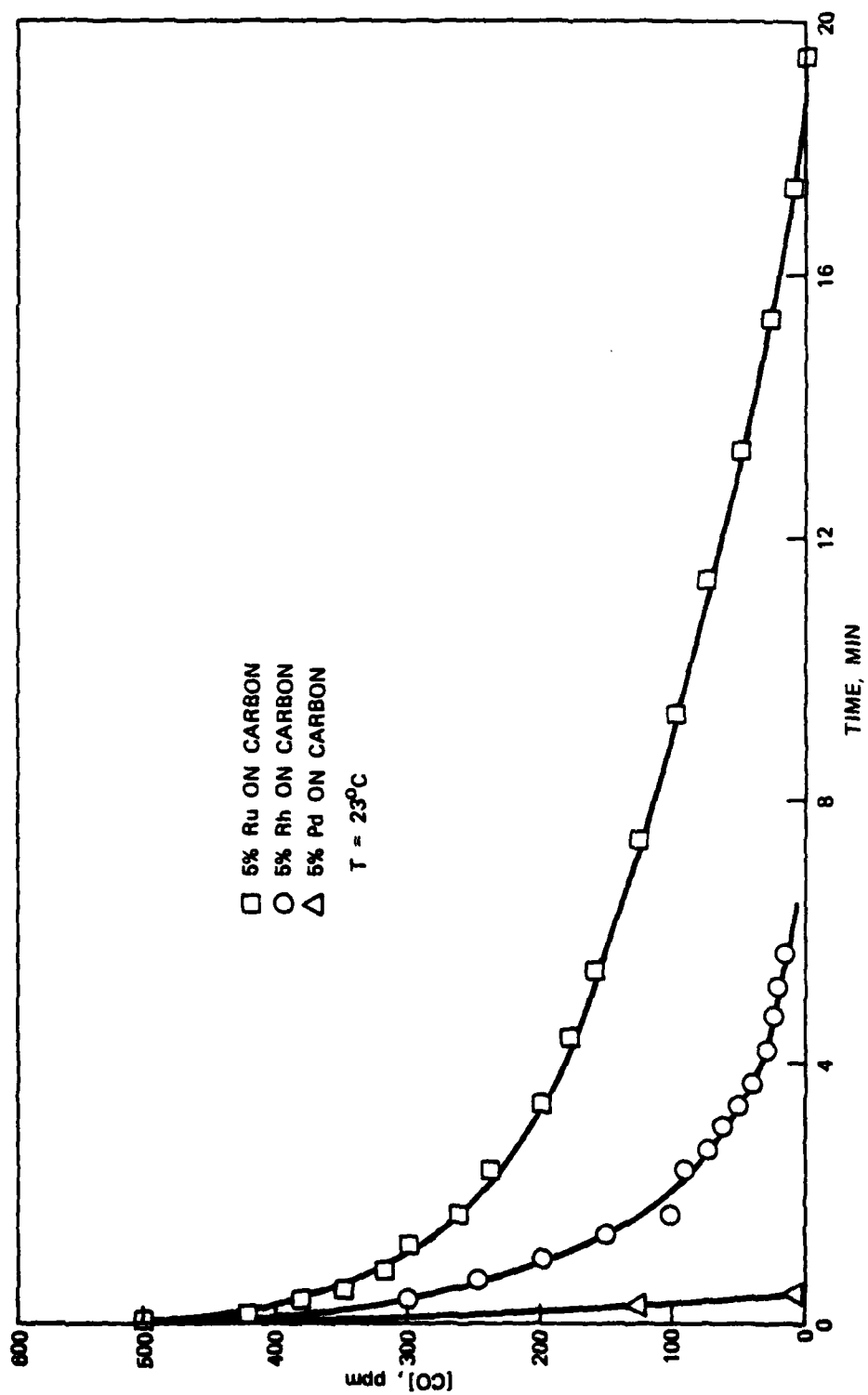


FIGURE 2. Removal of CO From CO/Air Mixture (ca. 500 cm<sup>3</sup>) by 1.0 g of Engelhard catalysts.

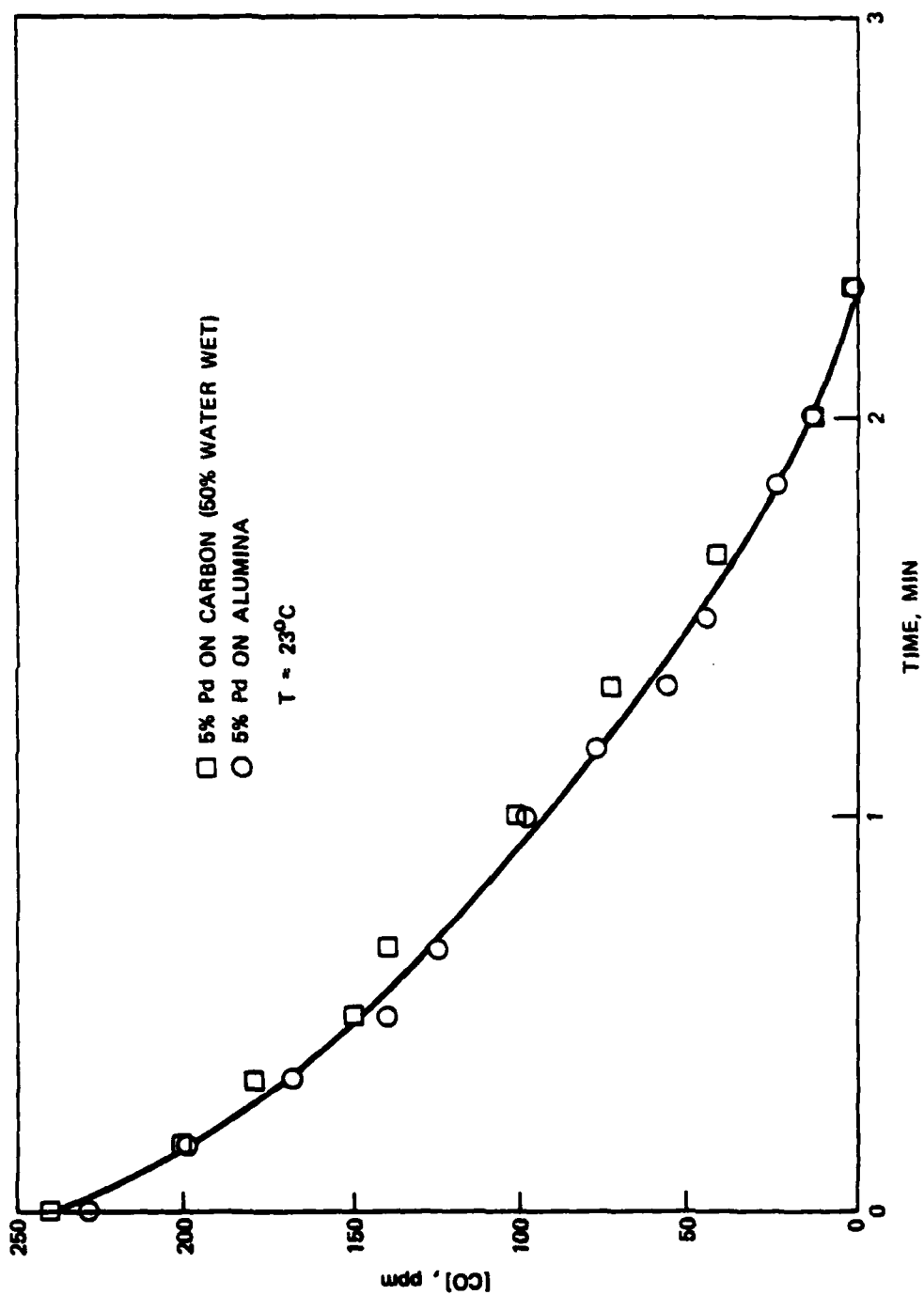


FIGURE 3. Removal of CO From CO/Air Mixture (ca. 6000 cm<sup>3</sup>) by 1.0 g of 5% Engelhard Palladium Catalysts.



Typical data for CO level vs. time are shown in Figure 4. As with CO/air mixtures, the process is not a simple first or second order reaction. Table 1 shows a comparison of removal rates for CO/air and CO/N<sub>2</sub>, for palladium catalysts. The slower rates for the CO/N<sub>2</sub> mixture would be expected in an oxidation process. It is possible that both oxidation and absorption processes are operative. Information on this matter could be obtained by analysis of the emergent gas for CO<sub>2</sub>. Time did not permit such analyses in this investigation, but qualitative and perhaps quantitative analysis could be accomplished by instruments such as the FTIR spectrometer now owned by NWC.

TABLE 1. Removal Rates of CO From CO/Air and CO/N<sub>2</sub> Mixtures by 1.0 g Engelhard Powdered Catalyst.  
(T = 25°C)

Catalyst	[CO]	Flow rate, cc/min	Time for passage of 1 system vol- ume, min	% of total CO re- moved on passage of first volume
I CO/air				
Pd/C	230	4000	1.5	80
Pd/C	240	5000	1.2	70
II CO/N <sub>2</sub>				
Pd/C	390	6200	0.95	11
Pd/C	200	6200	0.95	20
Pd/C	400	6500	0.90	23
Pd/Al <sub>2</sub> O <sub>3</sub>	440	7000	0.84	27
Pd/Al <sub>2</sub> O <sub>3</sub>	350	7000	0.84	24

#### TESTS OF ENGELHARD FIXED-BED CATALYSTS

A second batch of platinum-metal catalysts was obtained from Engelhard. These catalysts had a metal content of 0.5%. They included preparations of platinum, palladium, rhodium and ruthenium on 1/8-inch alumina pellets, and of palladium on 4-8 mesh granular carbon.

These catalysts were tested in the same manner as the powdered catalysts. Initial tests were run with 1.0 g of catalyst placed on the frit of a sintered-glass crucible. An advantage of the fixed-bed catalysts over the powdered catalysts soon became apparent -- the pellets and granules could not penetrate the frit, whereas the powders sometimes penetrated the frit during the circulation process and permeated the system.

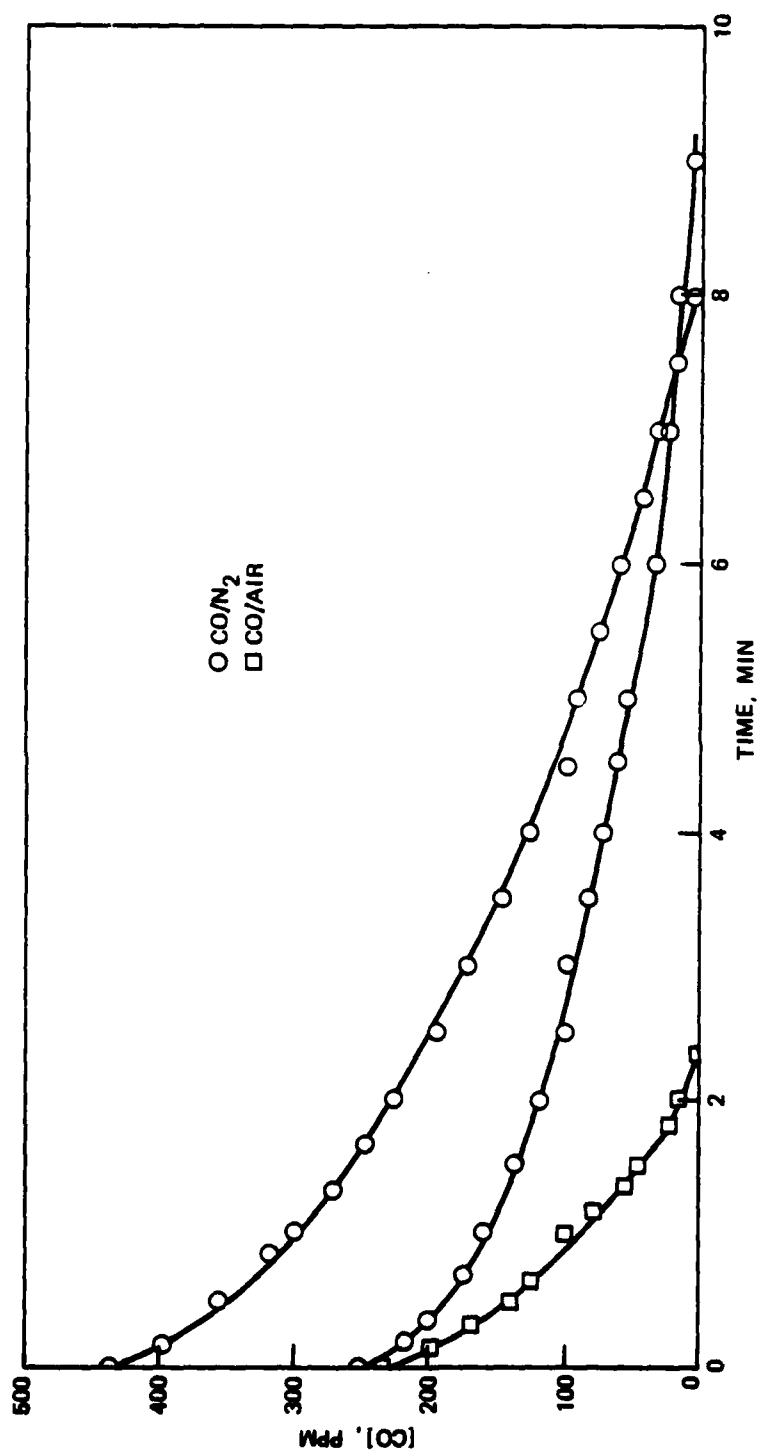


FIGURE 4. Removal of CO From CO/Air by 10% Solution of CuCl in 4M MEA, Saturated With NaCl. Bottom two curves show results for fresh solution; top curve is for same solution after six hours.

Initial tests were conducted with a small volume (ca. 500 cm<sup>3</sup>) of CO/air. Results are shown in Table 2. It is seen that the order of efficiency is

Pt > Pd/alumina > Pd/granulated carbon > Rh > Ru.

TABLE 2. Removal of CO From CO/Air Mixtures by 1.0 g Engelhard Pelletized or Granular Catalyst.

Catalyst	Initial [CO], ppm	Final [CO], ppm	Approximate time of run, sec
0.5% Pt/alumina pellets	400	230	20
	230	160	30
	96	0	<10
0.5% Pd/alumina pellets	400	260	30
	300	200	30
	210	120	20
	100	15	15
0.5% Pd/granular carbon	400	330	40
	245	190	15
	99	75	20
0.5% Rh/alumina pellets	400	350	10
	250	220	15
	100	88	20
0.5% Ru/alumina pellets	410	360	20
	250	230	10
	100	95	10

This is the same order of metals that was observed for the powdered catalysts. Comparative tests of three different palladium catalysts showed that the 0.5% Pd on alumina pellets had about the same efficiency as the 5% Pd on carbon powder, and was more efficient than the 0.5% Pd on granulated carbon. A series of comparative tests of corresponding powder catalysts was run; typical results are shown in Table 3. They indicate, in most cases, an appreciably greater efficiency for the powdered catalysts, as would be expected from the higher metal content, but the greater convenience of the pellets would seem to compensate for the difference in efficiency.

TABLE 3. Removal of CO From CO/Air Mixture by 1.0 g Engelhard Powdered Catalyst.

Catalyst	Initial [CO] ppm	Final [CO] ppm	~t
5% Pt/carbon powder	400	120	40 sec
	240	0	10 "
	100	0	<5 "
5% Pd/carbon powder	410	250	20 "
	250	150	20 "
	98	32	10 "
5% Pd/C, 50% water wet	410	100	40 "
	250	0	30 "
	100	0	10 "
5% Ru/carbon powder	400	360	20 "
	250	100	5 min
	100	75	3 "

A series of tests was run on different quantities of 0.5% Pd/alumina pellets, using the full volume of the apparatus (ca. 6000 cm<sup>3</sup>). The fraction of CO removed during the passage of a system volume through the catalyst was calculated from the analyzer readings and the flow rate. Results are shown in Table 4. The expected increase in CO removal rate with increasing weight of catalyst is observed.

#### TESTS OF SOLUTIONS OF COPPER(I)

Three different solutions of Cu(I) were prepared and tested:

1. An aqueous solution prepared by dissolving 6.3 g CuSO<sub>4</sub>·5H<sub>2</sub>O and 3 g NaCl in 75 ml 20% HCl. This solution is known to be a CO absorber.<sup>7</sup> The solution was stirred over copper metal shot until the color changed from the bright green of Cu(II) to the dark brownish-green of Cu(I) + Cu(II). [Some Cu(II) is always present in solutions of Cu(I), due to the disproportionation  $2\text{Cu}^+ = \text{Cu}^{2+} + \text{Cu}$  and the susceptibility of Cu<sup>+</sup> to air oxidation.]

<sup>7</sup> *Gmelin Handbook der Anorganischen Chemie*, Vol. 60B (1958), p. 234.

TABLE 4. Removal of CO by Pd/Al<sub>2</sub>O<sub>3</sub> Pellets.  
FR ~7,000 cm<sup>3</sup>/min; time for passage of one system volume ~0.85 min.

Wt. of catalyst, g	[CO], ppm	% removed, first pass	% of remainder removed		% of total removed by end of	
			2nd pass	3rd pass	2nd pass	3rd pass
2.0	300	17	12	11	27	35
5.0	410	38	41	37	63	77
	350	67	91	100	97	100
	250	56	54	100	80	100
	125	48	54	83	76	96
10.0	480	55	49	50	77	89
	300	68	100	...	100	...
	250	72	100	...	100	...

2. A solution containing 10% by weight of cuprous chloride (Fisher Scientific Company) in monoethanolamine (MEA)/water. MEA was 4 M, the concentration employed in the CO<sub>2</sub> scrubbers on submarines. Total copper concentration was 1.1 M. 10% CuCl in MEA has been mentioned as an industrial absorber.<sup>8</sup>

3. A solution with the same composition as 2., but saturated with sodium chloride (ca. 4 M).

All three solutions were kept under nitrogen and over copper shot until the tests were run. For the tests, about 50 ml of solution was placed in a glass vessel fitted with a bubbler. After the system was filled with a CO/air mixture, the mixture was bubbled through the solution, and the CO level was monitored via the analyzer. For some of the runs, the vessel containing the solution was immersed in an ice bath.

The results of the tests (Table 5) indicated that copper(I) solutions do absorb CO, but for the present purposes they are decidedly inferior to the catalysts tested. On the comparative tests with a small volume (ca. 500 cm<sup>3</sup>) of CO/air, the best results were obtained with fresh aqueous solutions of CuSO<sub>4</sub>/NaCl/HCl; this solution was comparable to the palladium/alumina pellet catalyst in ability to remove CO at initial concentrations ≤ 500 ppm. However, besides the obvious disadvantage of the need for large quantities of HCl, the solution also showed instability, with the Cu(I) oxidizing to Cu(II) in runs lasting more than 20 minutes, even when the solution was kept over copper shot.

Solutions of 10% CuCl in 4 M MEA showed little effect on the CO level. Solutions of 10% CuCl in 4 M MEA saturated with NaCl did show absorptive properties. In fact, the best single result in tests employing the full volume of the apparatus was obtained with a fresh solution of this composition (Figure 5). This effect of added chloride indicates that the best absorbing Cu(I) species is a chloro complex containing more than one chloride ion, as is known to be the case in aqueous HCl solutions.<sup>2</sup> However, disadvantages of the solution soon became apparent. The problem of air oxidation appears to be even more severe in MEA than in water. Upon dissolution of cuprous chloride in MEA, the dark blue color of Cu(II) appears immediately, and persists even after prolonged stirring of the solution over metallic copper. The Cu(I) ↔ Cu(II) equilibrium apparently is shifted toward Cu(II) when MEA molecules replace water molecules in the first coordination sphere of the copper ion. Only fresh solutions seem to be effective in removal of CO, and absorptive ability decreases rapidly with time as shown in Figure 5. As in the case of aqueous solutions, lowering the temperature increases CO absorption.

<sup>8</sup> W. Gluud, W. Klempt and H. Ritter, *Ber. Ges. Kohlentechn.*, Vol. 3 (1931), p. 525.

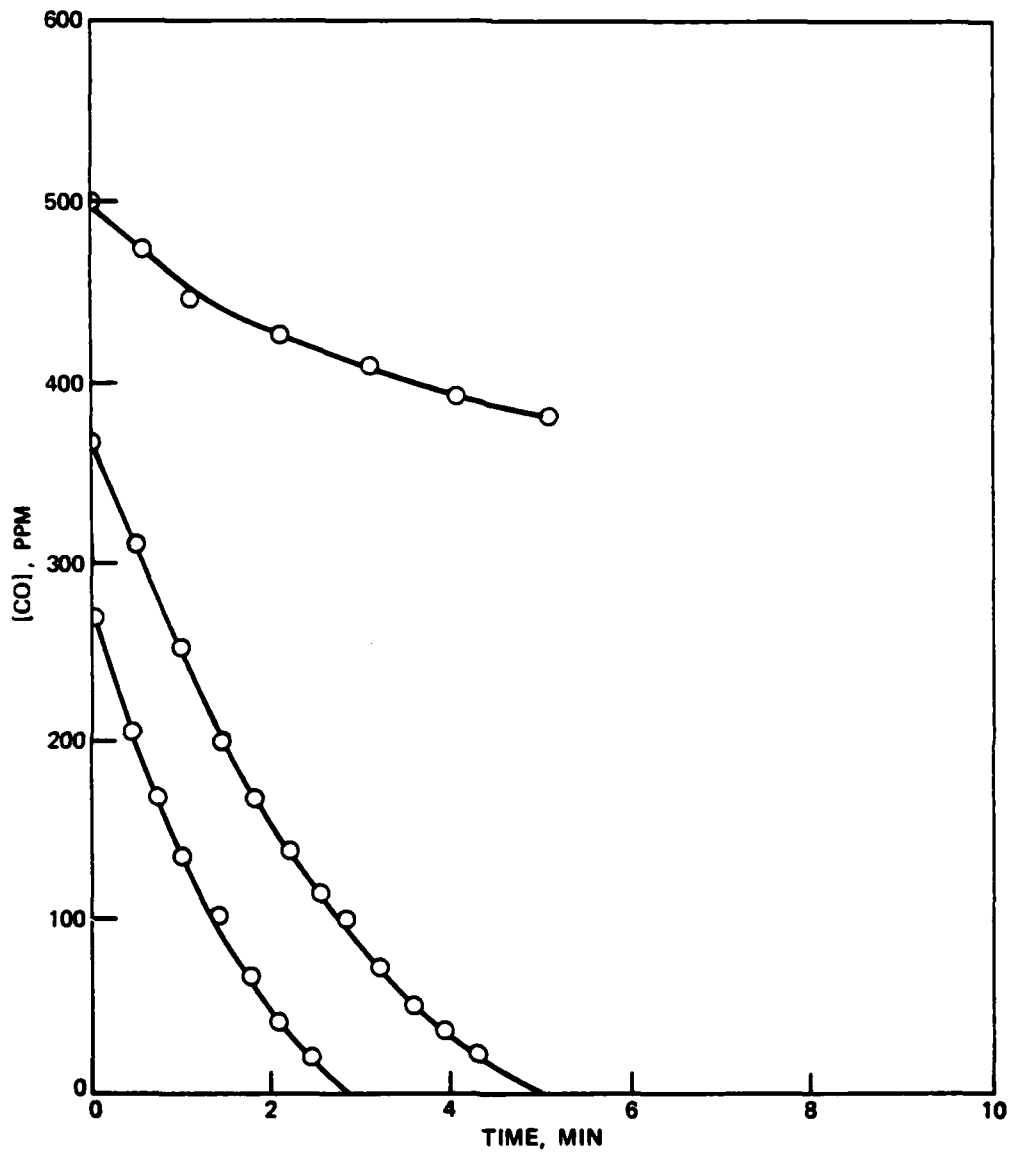


FIGURE 5. Removal of CO From CO/Air by 10% Solution of CuCl in 4M MEA, Saturated with NaCl. Bottom two curves show results from fresh solution; top curve is for same solution after 6 hours.

TABLE 5. Tests of Copper(I) Solutions.  
Flow Rate ca. 5000 cm<sup>3</sup>/min, T = 25°C.

Solution*	Initial [CO], ppm	Final [CO], ppm
b	400	360
c	400	300
a	400	250
b	360	340
c	360	220
b	250	250
c	250	200
a	250	150
c, cooled**	230	150
c	200	160
a, cooled	200	80
a, cooled	150	75
c, cooled	100	30
a, cooled	100	0
a	80	0

\* a - CuSO<sub>4</sub> (0.67 M) + NaCl (0.68 M) in 20% HCl, reduced with copper.  
b - 10% CuCl in 4 M MEA.

\*\* c - 10% CuCl in 4 M MEA, saturated with NaCl.  
In ice bath.

In several cases (example in Figure 6), a test with a catalyst was made immediately following a test with a solution. The increase in removal rate upon replacement of the solution by the catalyst is clearly evident.

#### DISCUSSION

Solutions of copper(I) do not appear to offer much promise for purposes of the problem at hand. Their industrial applications have been mainly to cases of absorption of large quantities of impurities from gases, rather than to reduction of low but physiologically dangerous atmospheric concentrations to safe levels. They would present



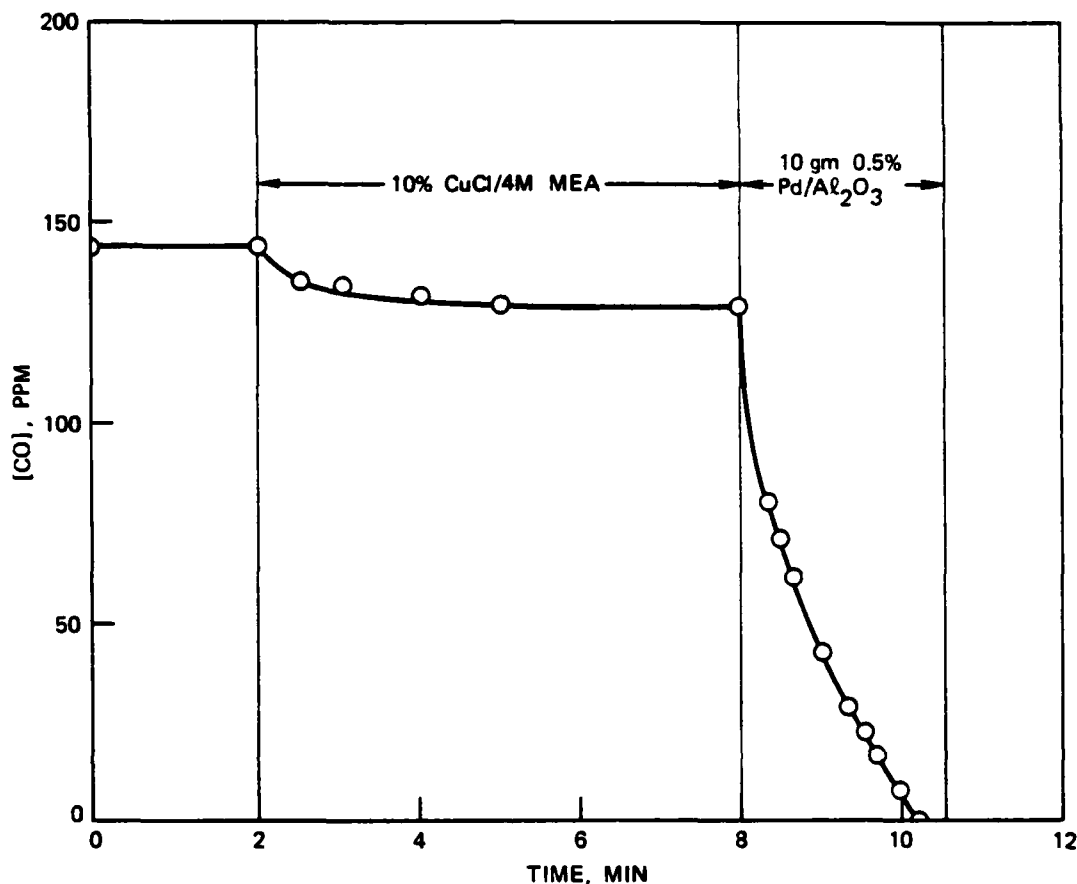


FIGURE 6. Removal of CO From CO/Air by 10% CuCl in 4M MEA and 0.5% Palladium on Alumina Pellets.

stability and storage problems due to their tendency toward air oxidation; this is especially true of MEA solutions. They are more effective at temperatures below normal room temperatures than at ambient temperatures. There is also the problem of regeneration, as the CO must ultimately be driven off from the cuprous complex by heating.

Of the types of CO removers tested in this investigation, i.e., powdered catalysts, pelletized catalysts and solutions, the most promising would seem to be the platinum and palladium pelletized catalysts. They could conceivably be deployed in the emergency canisters which are already used on submarines for removal of carbon dioxide during power failures. The powders, though perhaps more effective per unit weight, have the disadvantage of being harder to handle, and such fine powders would tend to permeate a circulation system. Also, the pellets with their lower metal content would probably offer a cost advantage.

The data of Table 4 permit a rough estimate of the amount of catalyst required to process a given volume of air, if certain simplifying assumptions are made. In the experiments conducted here, 10 g of palladium/alumina catalyst occupied 11 cm<sup>3</sup>. The density of pure alumina varies from 2.4 to 3.9 g/cm<sup>3</sup>; this yields an average value of 7.7 cm<sup>3</sup> for the open volume of the catalyst bed. Dividing this value by the flow rate of 7000 cm<sup>3</sup>/min, one obtains  $1.1 \times 10^{-3}$  min for the dwell time in 10 g of catalyst. The dwell time for other weights of catalyst would be directly proportional. If, for comparable initial CO concentrations, we plot the percent removal of CO on the initial passage of one system volume through the catalyst (Table 4) vs. the dwell time of that weight of catalyst (Figure 7), a plateau is seen to commence at around  $0.5 \times 10^{-3}$  min and 60% removal. Beyond this point, increasing the weight of catalyst produces only a slow rise in percent removal.

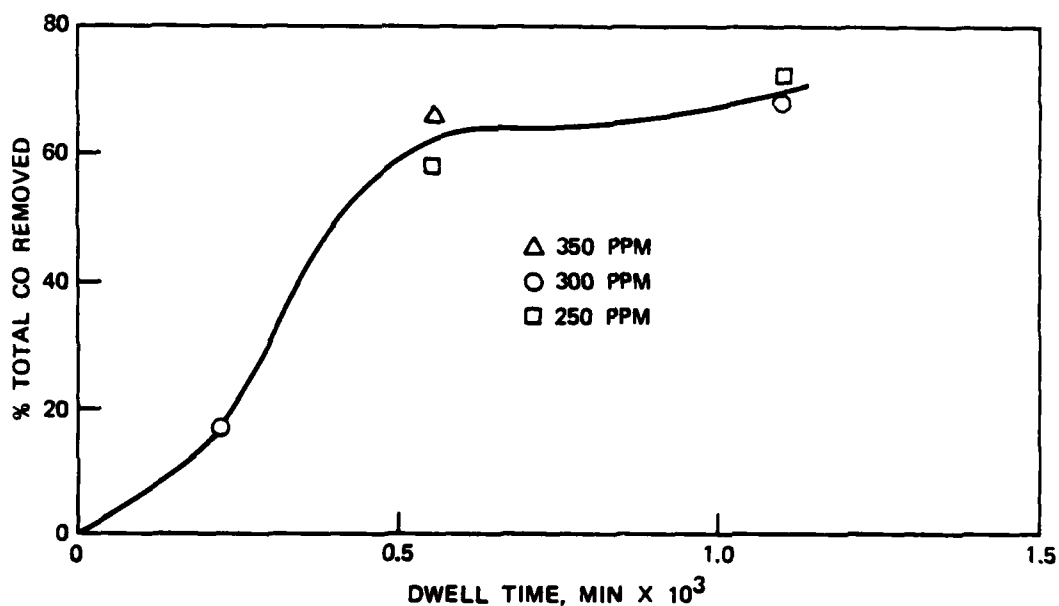


FIGURE 7. Removal of CO on First Passage of System Volume Through 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> Catalyst, vs. Dwell Time in Catalyst.

Let us now consider a volume of  $1000 \text{ ft}^3$  ( $28,000 \text{ l}$ ) of air containing 500 ppm CO, a value comparable to the concentrations studied in the present experiments. This value is tolerable by humans for 100 min. Removal of 60% of the total CO would reduce the level to 200 ppm, a concentration tolerable for 24 hr. Assume that this volume of air is passed in 100 min through a catalyst bed of sufficient volume to have a dwell time of  $0.5 \times 10^{-3} \text{ min}$ . This corresponds to processing 280 l per min. Since 10 g of catalyst has an open volume of  $7.7 \text{ cm}^3$ , the weight of catalyst needed to reduce the CO level to 200 ppm in 100 min would be  $280 \times 0.5 \times 10^{-3} \times 10 / (7.7 \times 10^{-3}) = 182 \text{ g}$ . A faster removal would require a proportionately larger weight, and a higher flow rate.

These calculations show that platinum or palladium pelletized catalysts should be usable to remove CO in many emergencies. More data are needed before the optimum materials and apparatus can be chosen.

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